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result in an improvement in device performance, revealing that Me-LPPP, in addition to MEH-PPV, is hole-limited with a Ca cathode. For conjugated polymer films, such as PAni, the improvement in quantum efficiency is due to an increase in the anode work function to 5.1 ± 0.1 eV, which results in a nearly ohmic contact. For nanoparticle monolayers, the improvement is due to an increase in the local electric field across the interface. This accelerating local electric field is induced by a net negative charge on the nanoparticle surface which results either from silicon hydroxyl groups on the SiO_2 surface or from electrons which are trapped at the interface between the conjugated polymer and nanoparticle.

In conclusion, we have shown that modification of the ITO electrode with SiO_2 nanoparticles can dramatically improve electroluminescence properties of polymer light-emitting devices (PLED). The charged nanoparticle surface, which serves as a carrier trap at low current densities, can induce a dipole moment across the electrode interface, effectively increasing the local electric field and promoting carrier injection. This effect enables the ability to improve PLED efficiency with a single monolayer without including additional polymer layers or modifying the electrode work function. Understanding the nature of the nanoparticle surface will clearly be critical to controlling and optimizing the performance of polymer/nanoparticle composite materials, offering further promise for innovative optoelectronic applications.

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Ordered Macroporous Materials by Colloidal Assembly: A Possible Route to Photonic Bandgap Materials**

By *G. Subramanian*, *Vinothan N. Manoharan*, *James D. Thorne*, and *David J. Pine**

Ordered macroporous materials with pore sizes in the sub-micrometer range have elicited much interest recently because of their applications in separations processes, catalysis, low dielectric constant materials, and lightweight structural materials. Macroporous oxides such as silica, titania, and zirconia as well as polymers such as polyacrylamide and polyurethane with well-defined pore sizes in the sub-micrometer regime have been successfully synthesized.[1–8] Apart from uses in structural and catalytic materials, the length scales of the pores confer these materials with unique optical properties. For instance, ordered macropores in a high refractive index matrix such as titania can be used to make photonic crystals with a photonic bandgap (PBG).[9] Applications of PBG materials include omnidirectional mirrors, waveguides, and suppression or enhancement of spontaneous emission.[9]

The key to making PBG materials is the requirement to make an ordered dielectric lattice of materials with a high refractive index contrast, n_2/n_1, where n_2 and n_1 refer to the larger and smaller refractive indices in the structure. The minimum contrast required depends on the lattice type and varies from 2.1 for a diamond lattice to about 3 for a face centered cubic (fcc) lattice.[9] Since n_1 cannot be less than 1, the highest refractive index contrast can be obtained by using a high refractive index material with an ordered array of voids. The range of wavelengths over which a crystal exhibits a stop band or omnidirectional bandgap is determined by the lattice spacing of the voids. Thus, to achieve a PBG in the visible, lattice spacings comparable to the wavelength of light are required.

A promising approach to the fabrication of PBG materials with stop bands at visible wavelengths involves the use of self-assembled templates. For synthesis of macroporous materials with pores in the sub-micrometer range, ordered

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arrays of colloids or emulsions have been employed as templates.[1–6,8] In this method, monodisperse particles such as emulsion droplets or latex spheres self-assemble to form an ordered three-dimensional array. The ordered arrays act as a scaffold around which a high refractive index matrix can be synthesized using wet chemistry techniques such as the sol–gel process. The templates are then removed either by heat treatment or dissolution with a solvent leaving a periodic array of holes in the dielectric matrix.

The advantage of the templating approach is that the self-assembly process assures three-dimensional order in the system. The crystal structure is predominantly cubic (either body centered cubic (bcc) or fcc) although other crystal structures can be obtained by using a binary mixture of colloids.[10] Since well-known techniques exist for producing colloidal particles with the desired sub-micrometer sizes, the lattice spacing can be varied over the entire visible spectrum. The three-dimensional order combined with the ability to produce lattice spacings in the sub-micrometer range make the templating approach a promising route to making PBG materials in the visible spectrum. Presently, the most promising candidate with a bandgap in the visible spectrum the is macroporous rutile phase of titania ($n \sim 3$) with a fcc lattice of pores.

Imhof and Pine[1,2] used non-aqueous monodisperse emulsions of isooctane in formamide as templates to synthesize titania. Monodisperse emulsions assemble spontaneously into an ordered lattice at sufficiently high volume fraction (>50 %). Gelation and removal of the droplets led to a macroporous amorphous titania gel. Subsequent heat treatment of the gel resulted in the formation of the pure rutile phase of titania. Unfortunately, the ordering of the pores was not sufficiently long ranged to produce a photonic bandgap.

In order to produce more highly ordered pores, colloidal crystalline assemblies of highly monodisperse polystyrene spheres have recently been used as templates in the synthesis of macroporous titania.[3,4] Alkoxide precursors were used to infiltrate the voids of an ordered array of polystyrene spheres. Gelation of the alkoxide and removal of the polystyrene by heat treatment to ~500 °C resulted in a macroporous ceramic with the pores ordered in a fcc lattice over tens of micrometers. An important limitation of this approach, however, is that there is significant shrinkage of the titania gel when the sample is heated to remove the polystyrene spheres. This results in severe cracking such that only powders are produced with particle dimensions of less than 0.5 mm. Achieving larger sample dimensions is highly desirable for many applications. A further limitation is that the titania framework produced by this approach is the lower refractive index anatase phase of titania ($n \sim 2.4$) instead of the high refractive index rutile phase ($n \sim 3$).

In this paper we present a simple and effective way of making macroporous materials that overcomes many of the limitations of the techniques described above. Most importantly, we demonstrate how it is possible to routinely produce much larger samples with dimensions of several millimeters or more. Our technique employs monodisperse polystyrene as templates but instead of using the traditional alkoxides as precursors to synthesize oxides, we employ ultrafine (<100 nm) colloidal particles of the oxides. The process involves mixing the monodisperse polystyrene dispersion with a colloidal dispersion of the desired oxide. On slowly evaporating the water in the mixture, the monodisperse polystyrene particles organize themselves in an ordered lattice due to a gradual increase in their concentration. The ultrafine oxide particles pack into the voids between the polystyrene particles. In effect, we produce a particulate gel of the oxide particles around the ordered polystyrene lattice. Subsequent removal of the polystyrene by calcination leads to an ordered macroporous material with the oxide particles forming the walls of the pores. We have made ordered macroporous silica and titania using this technique. The use of colloidal particles instead of alkoxides reduces shrinkage significantly and enables us to make well-ordered samples with dimensions of several millimeters. Moreover, by choosing suspensions where the particles have the desired crystalline phase, it should be possible to make ordered macroporous materials with a crystalline framework without resorting to high-temperature treatment. Such materials would have unique optical, electrical, magnetic, and catalytic properties. A further advantage of our method is that it is not limited to materials that can be produced by sol–gel chemistries. Thus, it has much wider applicability than previously described techniques for producing ordered macroporous materials.

Figure 1 shows scanning electron microscopy (SEM) micrographs of macroporous silica made with Snowtex ZL silica and a polystyrene dispersion with a particle diameter of 560 nm. The pores are highly ordered in a hexagonal array with the silica particles forming the walls of the pores. The holes connecting the pores are clearly visible and confirm the three-dimensional ordering of the structure. The hexagonal orientation is indicative of the (111) plane of the fcc lattice or the (001) hexagonal close packed (hcp) plane. Evidence of the fcc lattice is borne out by Figure 1c, which shows two different crystalline domains. The top right region shows a hexagonal ordering of pores while the bottom region reveals pores arranged in a square pattern. Figure 2 also shows the coexistence of the square and hexagonal symmetry over several tens of micrometers. The square arrangement of pores is consistent with the (100) plane of the fcc lattice and inconsistent with a hcp structure. It is also consistent with theoretical predictions[11,12] and experimental observations[13] that charge-stabilized colloids exhibit a fcc crystalline structure at high volume fractions. Thus both the SEM images of the pore structure and the phase behavior of charge-stabilized suspensions suggest a fcc structure of the pores. Nevertheless, since the SEM images reveal only the structure of a few crystalline planes, we cannot exclude the possibility of randomly stacked close-packed planes. Conclusive evidence of the structure can only be obtained by small-angle X-ray or light scattering.

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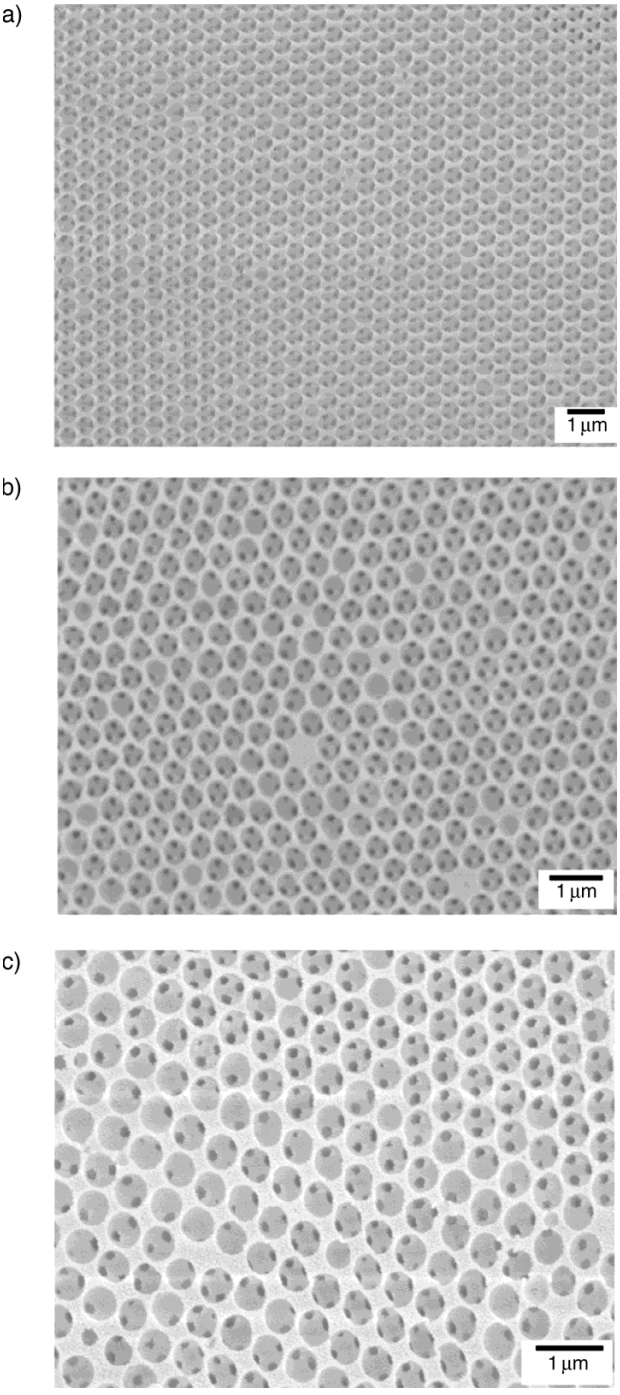

Fig. 1. SEM image of macroporous silica made with polystyrene latex and Snowtex ZL silica suspension. a) Ordered regions with hexagonal symmetry extending over 10 µm. b) Higher magnification image showing ordered, interconnected pores. c) Region showing both hexagonal and square symmetry.

The center to center distance between the pores is 525 nm and corresponds to a linear shrinkage of ~6 % with respect to the initial size of polystyrene. Previous experiments using polystyrene as templates and alkoxides as the oxide precursors invariably resulted in a linear shrinkage of 25–30 %.[3,4] Reaction of alkoxides with water to produce the oxide results in the production of large amounts of water and alcohol leading to a small fraction of the oxide material. Removal of the water and alcohol during drying and heat treatment contributes to a large shrinkage and cracking of the material into pieces with typical dimensions of a fraction of millimeter.[3,4] The use of colloidal particles significantly reduces the shrinkage as the particles pack to higher volume fraction in the voids of the ordered polystyrene particles.

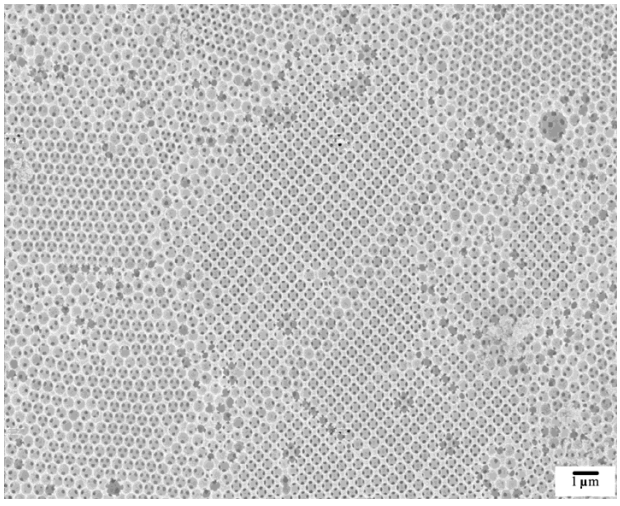

Fig. 2. Macroporous silica made with Snowtex OL and polystyrene latex. Image shows long-range ordering. Also note the presence of both hexagonal and square symmetry regions consistent with a fcc lattice of pores.

We can get an estimate of the amount of shrinkage expected using colloidal particles by the following argument. The polystyrene particles can be considered to form a close-packed array at a volume fraction of 74 %. The voids, which amount to 26 vol.-%, are filled by the colloidal metal oxide particles. Assuming the colloidal particles fill all the voids between the polystyrene particles and that the colloidal particles are packed to 64 vol.-% (corresponding to random close packing), the theoretical linear shrinkage expected is around 14 % assuming isotropic shrinkage of the sample. However, we see a linear shrinkage of ~6 %. The lower shrinkage could be attributed to incomplete densification of the particles. The linear shrinkage in our samples is a factor of two less than that achieved by using alkoxide precursors, enabling us to make samples that are several millimeters in length and width.

Similar results were obtained using titania dispersions. SEM micrographs of macroporous titania made with Nanotek titania dispersions are shown in Figure 3. The titania sample again shows an interconnected network of macropores with remarkable ordering in three dimensions. The pore sizes and the shrinkage are similar to the macroporous silica samples. Figure 3a shows the top surface of the titania sample at low magnification. The ordering of the pores can be observed over tens of micrometers corresponding to several unit cells of the porous structure. The pores appear smaller and not close packed because the surface slices

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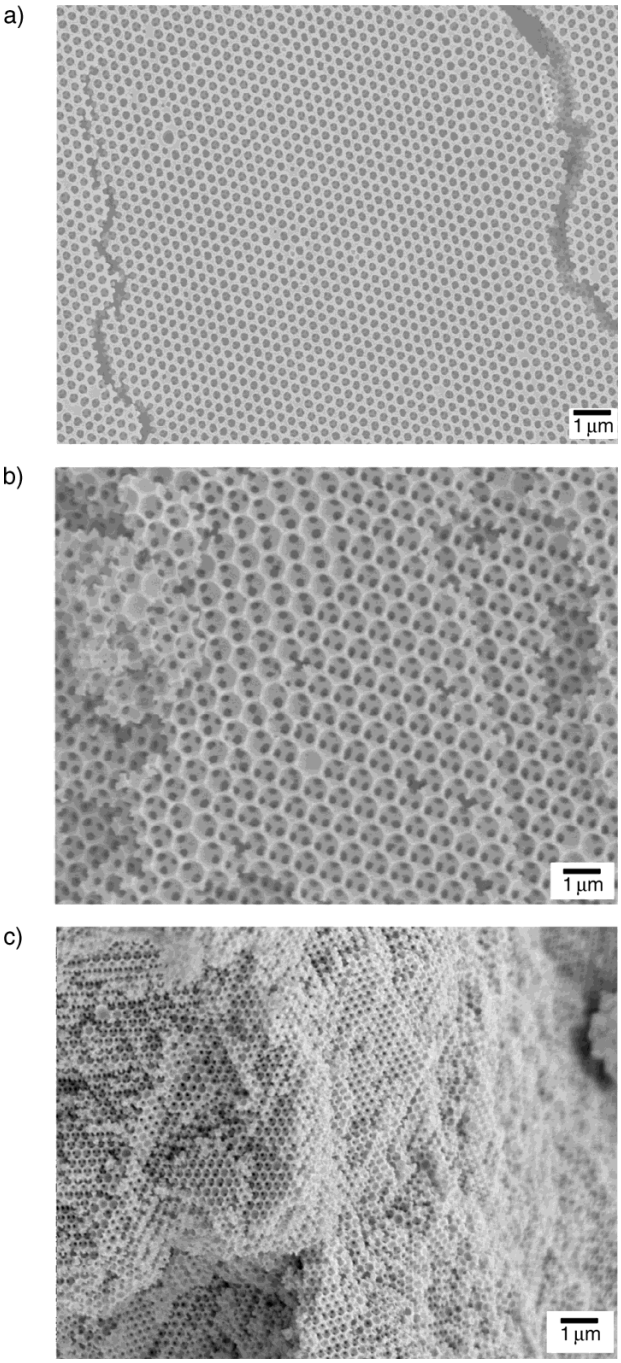

Fig. 3. Macroporous titania. a) Ordered pores on the top surface of sample. Pores do not appear to be close packed because the slice of the surface was not exactly through the center of the pores. b) Interior surface showing close-packed and interconnected array of pores. c) Fracture surface showing three-dimensional ordering of pores over tens of micrometers.

through only the top of the pores. That the pores are indeed close packed can be ascertained from Figure 3b, which shows the pore structure in the interior of the sample. Figure 3c shows the pore structure of a fractured surface, indicating the long-range ordering of the pores. Such long-range ordering of pores in a high refractive index matrix give rise to interesting optical properties, including the presence of stop bands.

The reflectivity spectra of three macroporous titania samples are shown in Figure 4. The peaks in reflectivity correspond to Bragg reflections arising from the ordered porous structure. The full width at half maximum of the peaks lies between 12 and 14 % and is related to the strength of the interaction between light and the ordered structure.

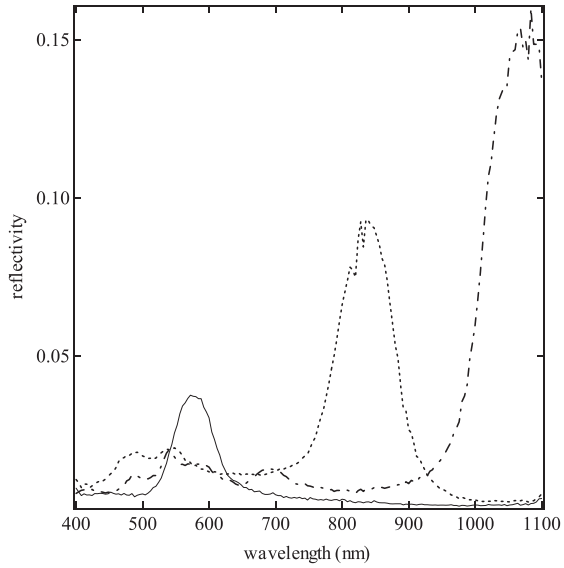

Fig. 4. Optical reflectivity spectra of macroporous titania. Peaks centered at 570, 840, and 1080 nm correspond to air holes of 320, 440, and 525 nm diameter, respectively. The reflected light was detected at an angle of $35 \pm 2°$ with respect to the incident beam.

The mechanism of formation of the macroporous materials can be understood as follows. The polystyrene–oxide dispersion on slow evaporation of water becomes gradually concentrated in polystyrene and the oxide particles. Since the polystyrene particles are monodisperse, they arrange into an ordered lattice as their concentration increases. Moreover, the polystyrene particles and the oxide dispersions are both negatively charged at the existing pH, leading to a stable suspension. This is a very important criterion, as rapid aggregation occurs when polystyrene with positively charged surface groups is used (heterocoagulation). The small oxide particles fill the voids between the polystyrene particles, gradually cementing the structure. The process appears similar to that of formation of some synthetic opals such as the Gilson synthetic opal as proposed by Simonton et al.[14]

We have shown that ordered macroporous materials can be made from colloidal particles with an ordered polystyrene latex as a template. The colloidal particles form a particulate gel around the template upon evaporation of water. Our method of synthesis has several advantages over the conventional sol–gel process using alkoxide precursors. Most important is the low shrinkage of the macroporous oxide achieved through use of the colloidal particles. This enhances the ability to produce relatively large samples that are several millimeters in dimension. Another

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advantage is the ability to directly use nanocrystalline colloidal oxide particles in our method (such as anatase titania). This obviates the need for high-temperature treatment to achieve crystallinity. Alkoxide precursors generally produce an amorphous oxide, which has to be heat treated to produce the desired crystalline phase. The simplicity of the chemistry of the process and the cost effectiveness also cannot be overlooked. The only requirements of the colloidal particles are that they have a charge similar to the polystyrene template in order to prevent heterocoagulation and that they are small enough to be incorporated into the void spaces between the polystyrene spheres. This also means that our method can be used to produce materials that cannot be fabricated by sol–gel chemistry. Thus, the variety of macroporous materials that can be made using the templating approach is greatly expanded.

As noted before, rutile has one of the highest refractive indices (with low absorption) in the visible spectrum. Macroporous rutile with pore dimensions of the order of the wavelength of light could potentially exhibit photonic bandgap effects at visible wavelengths. Hence there has been an intense interest recently in making macroporous rutile. However, attempts to stabilize the rutile structure in macroporous titania made by employing alkoxide precursors and with polystyrene latex templates have not proved successful. The pore structure is usually destroyed at the temperature of conversion to the rutile structure (~1000 °C).

We have attempted to convert our anatase titania particles to rutile by heat treatment to temperatures between 600 °C and 900 °C. At low temperatures (less than 750 °C) no significant conversion to the rutile phase was observed. For temperatures beyond 850 °C, we observed extensive grain growth of the particles, leading to the disruption of the macropores. We believe these grains to be rutile crystals but the reason for this extensive grain growth is not yet completely understood.

A more attractive approach would be to directly employ nanocrystalline rutile particles using our method to produce ordered macroporous rutile. This would eliminate the need for any heat treatment to achieve the rutile phase. We believe this approach has great promise for making useful photonic crystals with full optical bandgaps.

Experimental

Monodisperse polystyrene particles were made by a surfactant-free emulsion polymerization process using ammonium persulfate (Aldrich) as the initiator [15]. The particles were negatively charged (with SO_4^- groups on their surfaces) and the dispersions were extensively dialyzed in deionized water over a period of a few weeks. The deionized dispersions crystallized into an ordered lattice owing to the electrostatic repulsion between the particles. The polystyrene dispersions used in this work had a particle size of 560 nm at a solids concentration of 7.9 %.

The oxide dispersions used were silica and titania. Silica dispersions (Snowtex ZL and Snowtex OL) were a gift from Nissan Chemical Co. Snowtex ZL had a mean particle size of 80 nm at 40 wt.-% solids. The dispersion was stabilized at pH 9.5. Snowtex OL had a mean particle size of 50 nm at 20 wt.-% solids and at pH 3. At these pH values the silica particles are negatively charged (the isoelectric point of silica being at pH 2) and the mutual electrostatic repulsion between the particles provides effective stability against coagulation. The titania dispersion was purchased from Nanophase Technology and contained 55 wt.-% titania particles in water at pH 8.5. The median particle size of titania was 34 nm and the particles were crystalline consisting predominantly of anatase phase with a small fraction of rutile phase. Neither the silica nor the titania dispersions were monodisperse.

Samples were made by mixing the polystyrene dispersions with the silica or titania dispersions in a glass vial. The amounts of the dispersions were chosen such that the oxide particles could fully fill the voids between close packed polystyrene particles when the water in the sample evaporated. The glass vial, covered with a plastic film (Parafilm M) punched with a few holes, was dried in an oven at 60 °C. The parafilm ensures that the drying is not too rapid. We found that rapid drying resulted in disordered macroporous materials. After a few days, iridescent regions were observed in the top of the sample, which gradually extended through most of the sample as the drying proceeded. After complete drying the sample usually cracked into a number of pieces with typical dimensions of 2.5 mm × 2 mm × 0.6 mm. Moreover, we observed three distinct regions in the sample after drying. The top iridescent layer was primarily an ordered lattice of polystyrene particles with the oxide particles in the voids. The thin middle layer was also iridescent and consisted of pure polystyrene in a regular lattice. The bottom layer was not iridescent and consisted of pure oxide particles. The top iridescent layer was carefully scooped off the walls and heat treated in a furnace to remove the polystyrene template. Heating was done in an air atmosphere at 450 °C at a heating rate of 2 °C min^{-1}. The heat-treated samples still retained the iridescence and shape of the initial pieces. The samples were then characterized by SEM to probe the porous structure.

SEM was performed on a JEOL 6300 field emission microscope. The samples for SEM were coated with a 500 Å layer of Au/Pt to make them conductive. An acceleration voltage of 3–5 kV was typically used.

Optical reflection spectra of macroporous titania samples were measured to probe the existence of stop bands. The incident light emerged from a monochromator that is fed by a Xe arc lamp. The bandwidth of light from the monochromator was ~2 nm. The reflected light was detected with a photodiode placed at an angle of 35 ± 2° with respect to the incident light.

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Note added in proof: While this paper was in review, we became aware of the report by Subramania et al. (*Appl. Phys. Lett.* **1999**, *74*, 3933) that describes a technique for making films of macroporous titania that is very similar to our own procedure.

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